ELECTRON SPIN RESONANCE IN THE PHASE TRANSITION REGION OF SOLID SOLUTIONS EXHIBITING FERROELECTRICITY AND STRONG MAGNETISM

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The electron spin resonance method was used to determine the temperatures of the ferroelectric and magnetic phase transitions in solid solutions of the systems $PbFe_{2/3}W_{1/3}O_3$-Pb_2YbNbO_6 and $PbTiO_3$-$Sr_{0.3}La_{0.7}MnO_3$, which exhibit ferroelectricity and strong magnetism. It was established that, near a ferromagnetic or a ferrimagnetic transition, the temperature dependence of the resonance line width ΔH had a sharp minimum. A considerable anomaly was observed also in the $\Delta H(T)$ curve in the region of the ferroelectric transition.

PHASE transitions in materials exhibiting ferroelectricity and strong magnetism can be detected and investigated by the electron spin resonance method. The method is particularly useful in the case of samples having high conductivity, poor quality of the ceramic, or low content of paramagnetic ions, when dielectric and magnetic measurements are difficult.

Ferroelectric substances with ferromagnetic and ferrimagnetic properties exhibit ferromagnetic resonance over a wide range of temperatures in the presence of paramagnetic ions of sufficiently long relaxation times. Characteristic changes in the electron structure take place at the phase transition points and these should lead to changes in the resonance spectra. We used this method to investigate the ferroelectric and the ferromagnetic or ferrimagnetic phase transitions in a series of perovskite-structure solid solutions of the systems $PbFe_{2/3}W_{1/3}O_3$-Pb_2YbNbO_6 and $PbTiO_3$-$Sr_{0.3}La_{0.7}MnO_3$, which were investigated by us earlier using other methods.[1,2]

The electron spin resonance was investigated using an instrument of the ÉPA-2 type at a frequency of 9000 MHz. A powder sample was placed in a quartz ampoule which was inserted in a rectangular resonator. The resonance spectrum of all the samples was in the form of a single line several hundred oersteds wide, which was typical of ferrites. We investigated the behavior of the resonance absorption line as a function of temperature. The temperature measurements were carried out in a stream of dry gas at a given temperature. The resonance line width ΔH was determined with an accuracy of 3%; the temperature was measured to within 2–3°.

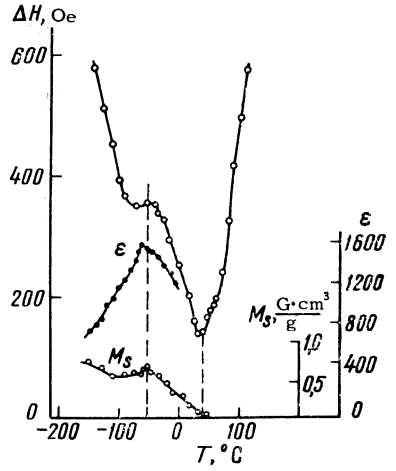

FIG. 1. Temperature dependence of the resonance absorption line width ΔH for the 90 mol. % $PbFe_{2/3}W_{1/3}O_3$ + 10 mol. % ½(Pb_2YbNbO_6) composition, compared with the temperature dependences of the permittivity ϵ and of the spontaneous magnetization M_S, taken from [1].

The characteristic temperature dependence of ΔH of samples of the system $PbFe_{2/3}W_{1/3}O_3$-Pb^2YbNbO_6 is shown in Fig. 1. A characteristic feature of the $\Delta H(T)$ curve is the narrowing of the line in the ferrimagnetic region when the temperature is increased right up to the ferrimagnetic transition point in the region of 40°C, where the width increases sharply. Such a dependence is characteristic of rare-earth iron garnets and is explained in [3,4] by the presence of two magnetic sublattices: the iron and rare-earth ion sublattices, the latter having very short relaxation times ($\approx 10^{-12}$ sec). According to Kittel et al.,[3,4] the line width is proportional, over a certain range of temperatures, to the magnetization of the rare-earth ion sublattice. Far from saturation, this

magnetization, and therefore the line width, decrease when the temperature is increased. The sharp rise of the $\Delta H(T)$ curve in the region of a magnetic transition is explained by the enhancement of the magnetization fluctuations in the iron sublattice at this temperature. We can assume that similar processes also take place in our case (in the presence of Fe and Yb sublattices).

An important feature of the $\Delta H(T)$ curve is the anomaly between −50 and −70°C, corresponding to the ferroelectric transition temperature. The reason for this anomaly is, evidently, a change in the state of the paramagnetic ions due to the appearance of strong electric fields [5] and the change in the symmetry of the environment below the Curie point. Similar anomalies have been observed in the ferroelectric and ferrimagnetic transition regions in other samples of this system and they are in fairly good agreement with the results of the dielectric and magnetic measurements (Fig. 1). The change in the spectrum in the ferroelectric transition region illustrates the interrelations between the electric and magnetic properties of a substance which exhibits both ferroelectricity and strong magnetism.

Figure 2 shows the dependence $\Delta H(T)$ for some samples of the system $PbTiO_3$-$Sr_{0.3}La_{0.7}MnO_3$. The sharp minima in the $\Delta H(T)$ curves correspond to the ferromagnetic transitions identified from the magnetic measurement data. The rise in ΔH at the transition point is evidently due to, as in ferrites, an enhancement of the magnetization fluctuations in the lattice (Mn ions).

It has been reported earlier [2] that, in the case of compositions close to $PbTiO_3$ and having low concentrations of paramagnetic ions, the determination of the phase transitions is difficult because the magnetic moments are small. However, the anomalies in the $\Delta H(T)$ curves of such compositions (65 and 78% $PbTiO_3$) are very clear. Using the method described here, we detected a series of magnetic transitions in the systems $PbFe_{2/3}W_{1/3}O_3$-Pb_2YbNbO_6-$BiFeO_3$ and

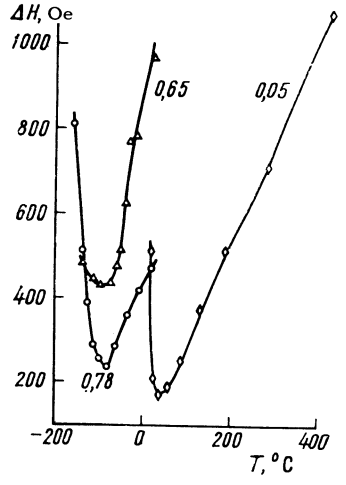

FIG. 2. Temperature dependence of the resonance absorption line width ΔH for some compositions of the system $PbTiO_3$-$Sr_{0.3}La_{0.7}MnO_3$. The numbers alongside the curves indicate the $PbTiO_3$ content.

Pb_2CoWO_6-$BiFeO_3$. The results obtained indicate that the spin resonance method is an effective means of investigating electric and magnetic phase transitions in substances exhibiting ferroelectricity and strong magnetism, particularly when these transitions are difficult to determine by other methods.

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